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Properties of multilayer gallium and aluminum doped ZnO(GZO/AZO) transparent thin films deposited by pulsed laser deposition process

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Abstract: Multilayer gallium and aluminum doped ZnO (GZO/AZO) films were fabricated by alternative deposition of Ga-doped zinc oxide(GZO) and Al-doped zinc oxide(AZO) thin film by using pulsed laser deposition(PLD) process. The electrical and optical properties of these GZO/AZO thin films were investigated and compared with those of GZO and AZO thin films. The GZO/AZO (1:1) thin film deposited at 400 °C shows the electrical resistivity of 4.18×10^{-4} Ω·cm, an electron concentration of 7.5×10^{20} /cm^3, and carrier mobility of 25.4 cm^2/(V·s). The optical transmittances of GZO/AZO thin films are over 85%. The optical band gap energy of GZO/AZO thin films linearly decreases with increasing the Al ratio.

Key words: multilayer; thin films; Ga-doped zinc oxide; Al-doped zinc oxide; pulsed laser deposition

1 Introduction

Most of the research on the transparent conducting oxide (TCO) thin films has been focused on ITO because the films have high electrical conductivity and high transmittances in the visible region. Lately, high price and shortage of indium have accelerated the search for new alternative transparent conducting oxide materials to replace ITO. Among new alternatives for ITO thin films, the zinc oxide based thin films have received much attention from many research groups since zinc oxide is abundant and relatively inexpensive compared with commonly used indium compound and have excellent electrical, chemical, and optical properties for potential applications in transparent electrodes, solar cells, and optoelectronic devices[1−6].

ZnO is very well known n-type semiconductor with wide band gap energy of 2.3−2.4 eV. Aluminum, indium, and gallium have been reported as effective n-type dopant to increase the electrical conductivity of pure zinc oxide[7−10]. Although aluminum is the most widely used dopant of the zinc oxide thin film, gallium can be an alternative dopant due to its inertness and oxidation resistance.

Several deposition techniques have been used for ZnO based transparent conducting thin films such as RF sputtering, MOCVD, reactive evaporation, and pulsed laser deposition (PLD) method[11−12]. Among these various techniques, sputtering has been the most commonly used technique to deposit TCO films for display applications. Pulsed laser deposition method has also been widely adopted because it has several advantages over other thin film techniques such as the reproducibility of the thin film composition even for a multi-component system, and multi-layers thin films of different target compositions[13−15]. The structure and properties of doped ZnO thin films may depend on deposition technique as well as compositional change. Lately, multilayer transparent conducting oxides with IZO/Al/GZO thin film layers were fabricated to improve electrical conductivity of the thin films[16]. In this study, we deposited multilayer of GZO/AZO thin films by pulsed laser deposition process. The electrical and optical properties of GZO/AZO multilayer thin films were investigated and compared with GZO and AZO thin film with the same amount of doping concentration.

2 Experimental

In this study, multilayer GZO/AZO films were fabricated by alternative deposition of GZO and AZO films with GZO and AZO targets by using pulsed laser deposition process and electrical and optical properties of these films were compared each other. The targets for GZO and AZO thin films were prepared by conventional

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ceramic method. The doping concentrations of AZO and GZO targets were 2% (molar fraction) of Al and 2% (molar fraction) of Ga, respectively. Stoichiometric proportions of ZnO (Aldrich 99.99%), Al_2O_3 (Aldrich 99.9%), and Ga_2O_3 (Aldrich 99.9%) powders were mixed and pelletized to disk with 1.5 cm in diameter and subsequently heat-treated at 1 350 °C in air for 3 h. The overall compositions of multilayer GZO/AZO thin films were controlled by varying the deposition time. For example, multilayer GZO/AZO(molar ratio of 1.5:0.5) thin film with doping concentration of 1.5% Ga (molar fraction) and 0.5% Al (molar fraction) was prepared by depositing GZO thin films for 1.5 min and AZO thin films for 0.5 min, repeatedly. Total deposition time was 8 min for all samples.

An Nd:YAG laser beam (λ=355 nm, Quantel Brilliant B) was used by ablating the target at various substrate temperatures. The energy density of the laser beam and the repetition rate were 1.5−2.0 J/cm^2 and 5 Hz, respectively. Pulsed laser deposition chamber was evacuated below 266×10^{-6} Pa, and the working pressure was controlled to about 565×10^{-4} Pa with 5 cm^3/min flowing oxygen. The distance from the target to substrate was fixed to 60 mm.

To investigate the effect of the substrate temperature on the crystal structure and the physical properties of multilayer thin films, the substrate temperatures were varied between 100 °C and 500 °C. The deposition time was 8 min for all samples. The thickness of the film was measured by using a stylus profiler (DI instrument DEKTAK 3) and SEM, and average thickness was approximately 150 nm. The crystal structure and the crystallinity of the films were monitored by using an X-ray diffractometer with Cu K_α radiation (λ=1.540 5 Å, Rigaku D/Max 2000H). The surface morphologies and film roughness were examined by using an SEM (Hitachi S-4800) and atomic force microscope (AFM, AP0190), respectively. The electrical resistivity, Hall mobility, and carrier concentration of the films were measured by utilizing a van der Pauw configuration (Ecopia, HMS-3000, Korea). The optical transmittances were measured by using an UV-visual spectrometer (Varian Inc, Cary 500) in the visible range of 300−800 nm.

3 Results and discussion

Fig.1 shows the X-ray diffraction patterns of the multilayer GZO/AZO(1:1) thin films deposited at various substrate temperatures. The GZO/AZO thin films deposited at temperatures below 100 °C were amorphous while well crystallized polycrystalline phases could be obtained at temperatures above 200 °C. GZO/AZO multilayer thin films reveals strong (002) and (004) peaks, which implies that the ZnO thin films grow with *c*-axis preferred orientation normal to the glass substrate shown in other AZO and GZO thin films. The full width half maximum (FWHM) value was about 0.23° when deposition temperature was 400 °C and the quality of thin films increased with increasing temperature. Fig.2 shows the dependence of electrical resistivity of GZO/AZO(1:1) multilayer thin film as a function of the substrate temperature. The resistivity of the samples decreased sharply as the substrate temperature was increased from 100 °C to 200 °C, and reached a broad minimum at 350−400 °C and slightly increased for further increase in substrate temperature. Based on those data, GZO/AZO multilayer thin films with various compositions were deposited at 400 °C.

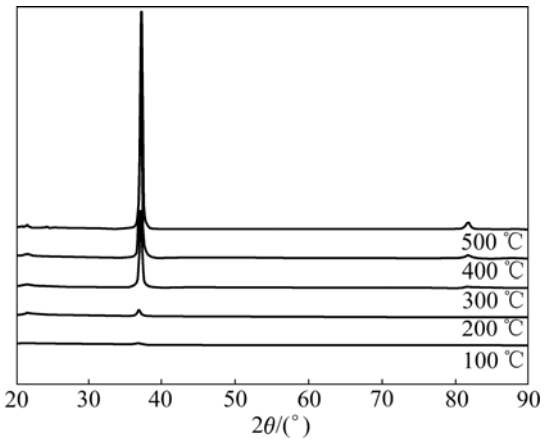

Fig.1 X-ray diffraction patterns of GZO/AZO(1:1) multilayer thin films deposited at various substrate temperatures

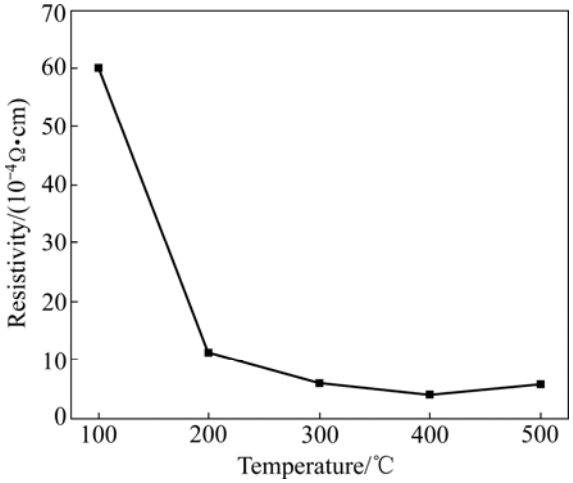

Fig.2 Dependence of resistivity of GZO/AZO(1:1) multilayer thin films on substrate temperature

The dependences of electrical resistivity, carrier concentration, and hall mobility of GZO/AZO multilayer thin films on Ga to Al doping concentration are shown in Fig.3. It is noted that total doping concentration of (Ga+Al) was maintained at 2% (molar fraction) and doping concentrations were varied by changing the

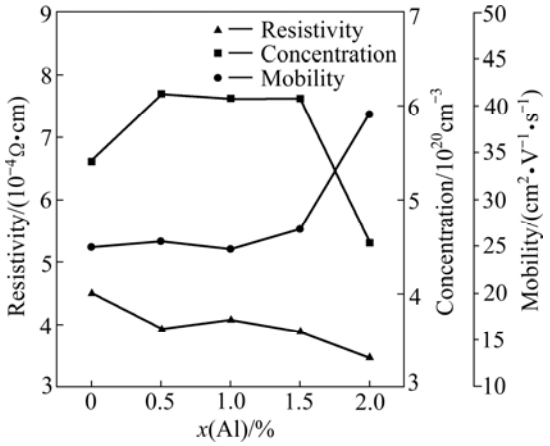

Fig.3 Dependence of resistivity, carrier concentration, and mobility of GZO/AZO thin film on Al-doping concentrations (Total doping concentrations of Al and Ga were fixed to 2% (molar fraction) for all samples. Substrate temperature of samples was 400 °C)

alternative deposition time with GZO and AZO ceramic targets. The electron concentrations of GZO/AZO thin films are slightly higher than those of AZO and GZO, and varied from 4.6×10^{20}/cm^3 of AZO to 6.1×10^{20}/cm^3 of GZO/AZO(1:1), which implies that Ga and Al ions are more easily ionized when Ga and Al are simultaneously doped. The mobilities of GAO/AZO thin films were lower than those of GZO and AZO. As a result, the resistivity of the GZO/AZO multilayer thin films shows no appreciable change with doping ratio.

Fig.4 represents the optical transmittance spectra of GZO/AZO multilayer thin films deposited at 400 °C with various molar ratio of Al to Ga and pure ZnO thin film. As shown in Fig.4, the average optical transmittances were over 85% at the wavelength from 400 to 800 nm for all samples, and absorption edge shifts were clearly

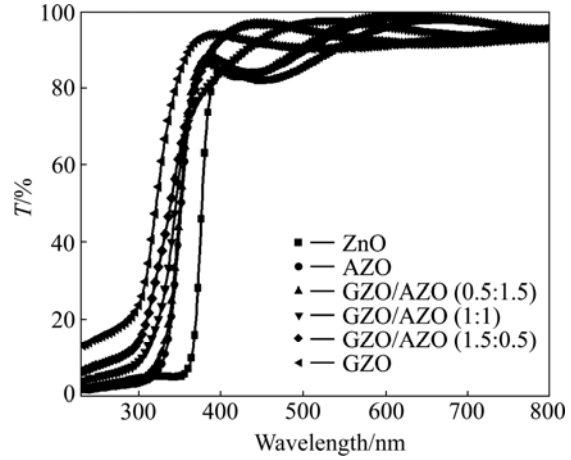

Fig.4 Optical transmittance spectra of GZO/AZO thin films as function of wavelength (Total doping concentrations of Al and Ga were fixed to 2% (molar fraction) for all samples. Substrate temperature of samples was 400 °C)

observed toward higher energy, i.e. shorter wavelength, as the Ga doping increased. The absorption edge shift of doped thin films compared with the ZnO thin films can be explained by Burstein-Moss effect in which carrier higher of concentration in doped films fill the electronic states of the conduction band [17].

The band gap energy E_g can be calculated by extrapolating the linear part of the plot of α^2 vs $h\nu$. Fig.5 shows the optical band gap calculated from the transmittance data using TAUC's plot $(\alpha h\nu)^2=C(h\nu-E_g)$, where α is optical absorption coefficient, E_g is band-gap energy, and $h\nu$ is photon energy[18]. The optical band gap of energy of pure ZnO was 3.27 eV, and the band gap energy of GZO/AZO thin films linearly decreased as the Al ratio increased from 3.82 eV for GZO, 3.62 eV for GZO/AZO (1:1), and 3.52 eV for AZO, as shown in Fig.6.

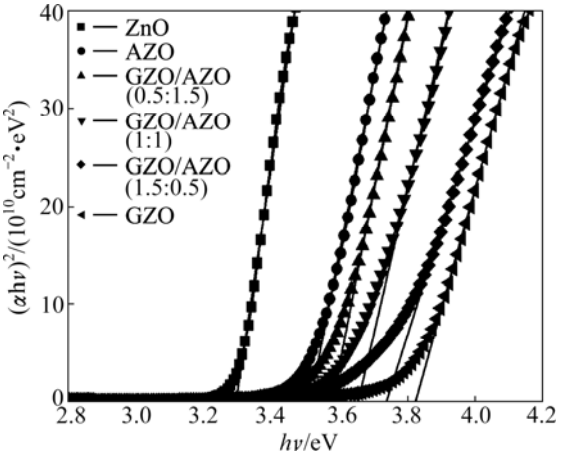

Fig.5 Optical band gaps of AZO/GZO thin films with various Ga/(Al+Ga) doping ratio (Total doping concentrations of Al and Ga were fixed to 2% (molar fraction) for all samples. Substrate temperature of samples was 400 °C

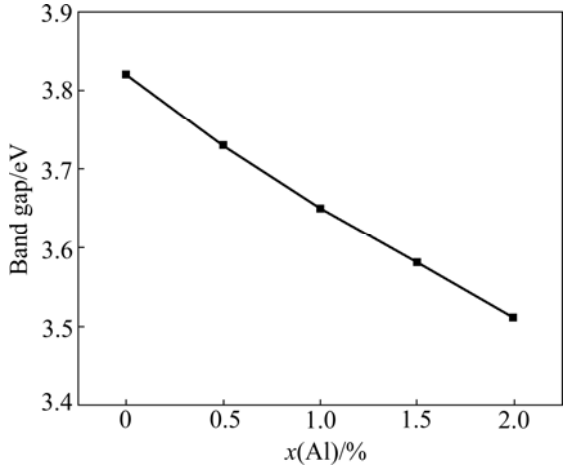

Fig.6 Optical band gaps of GZO/AZO thin films with various Al/(Al+Ga) doping ratio (Total doping concentrations of Al and Ga were fixed to 2% for all samples. Substrate temperature of samples was 400 °C)

This trend is in good agreement with the previous results of PARK et al[19]. From this result we may suggest that Ga ions are more easily ionized than Al ions, but this assumption is not well agree with the electron concentrations data shown in Fig.3.

Fig.7 shows the AFM images of GZO/AZO(1:1) multilayer thin film deposited at 400 °C and GAZO thin film which was prepared with Al and Ga co-doped target as a single layer. The R_{ms} and R_a values of surface morphology of GZO/AZO(1:1) thin film were found to be 2.6 nm and 2.0 nm, which indicates that the surface of GZO/AZO films are relatively uniform compared with GAZO thin film.

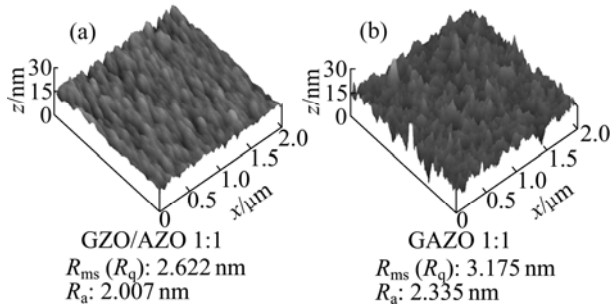

Fig.7 AFM images of GZO/AZO(1:1) thin films (a) and GAZO thin films (b) deposited at 400 °C

4 Conclusions

1) Multilayer transparent conducting oxides GZO/AZO thin films were fabricated by alternative deposition of GZO and AZO thin films by using pulsed laser deposition process.

2) The GZO/AZO(1:1) thin films deposited at 400 °C show the electrical resistivity of 4.18×10^{-4} Ω·cm, an electron concentration of 7.5×10^{20} cm^{-3}, and carrier mobility 25.4 $cm^2/(V\cdot s)$.

3) The GZO/AZO thin films begin to crystallize at 100 °C, and a well crystallized phase could be obtained at 300 °C. The optical transmittances of GZO/AZO thin films are over 85%.

4) The optical band gap energy of GZO/AZO thin films linearly decreases as the Al ratio increases from 3.82 eV for GZO, 3.62 eV for GZO/AZO (1:1), and 3.52 eV for AZO.

Acknowledgement

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